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ASSESSMENT OF SURFACTANT-ENHANCED BIOREMEDIATION OF SOILS CONTAINING STRONGLY SORBING HYDROCARBONS

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13. ABSTRACT *(Maximum 200 words)*

Biodegradation of phenanthrene was studied in soil slurry reactors in the presence and absence of a surfactant solution. Results showed that the presence of surfactants slowed the initial biodegradation rate of phenanthrene, but increased the total mass of phenanthrene degraded over a four day period by 30%. A mathematical model was developed to simulate the dynamics of the biodegradation of low solubility hydrocarbons in the presence of soils and surfactants. Processes such as the desorption kinetics of the hydrocarbon from soil, the sorption of the surfactant onto soil and its effect on the sorption of the hydrocarbon, and the bioavailability of the dydrocarbon in different phases of the system are included in the model formulation. The experimental results were measured independently. The model was used to investigate the effect on the overall biodegradation of phenanthrene due to different operating conditions. simulation results showed that there is a system-specific optimum surfactant concentration, above which bioremediation is hindered.

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Surfactant-Enhanced Bioremediation
Technical Report for July 1996 to June 1997
Air Force Office of Scientific Research Grant F49620-94-1-0327.

Overview

Removal of hydrophobic organic compounds (HOC) from contaminated soils is severely affected by the low HOC water solubility and high partitioning onto the soil matrix. Surfactants have been found to be effective in solubilizing hydrophobic contaminants from soil surface (see Figure 1). Solubilization depends on the type and dose of the surfactant, the hydrophobicity of the contaminant, the surfactant-soil interaction [Edwards et al. (1994a,b,c, 1992a,b, 1991); Aronstein at. al. (1991); Liu et. al. (1990)], and the time that the contaminant has been in contact with the soil [Vignon and Rubin (1989)]. The same traits which result in the low HOC water solubilities also result in low HOC biodegradation rates. Over the last few years attention has been focused on increasing the bioavailability of HOC with the addition of surfactants [e.g., Aronstein et al. (1991); Edwards et al. (1992b); Guha and Jaffé (1996a,b); Guha (1996)]. While research has indicated that surfactants can enhance the solubility and bioavailability of hydrophobic compounds, the question remains as to whether surfactant-enhanced bioremediation is a feasible process for remediation of contaminated soils.

Objective

The combination of surfactant-enhanced HOC solubilization and bioavailability shown in Figure 1 has the potential of enhancing the biodegradation of HOC; however, the interactions between the HOC solubilization and bioavailability, and effects of HOC sorption/dissolution, need to be examined in order to determine the feasibility of the surfactant-enhanced bioremediation (SEB) process. The objective of the current research is to increase our understanding of the SEB process and to identify operational regimes where the SEB process is applicable. This objective will be met by, (a) developing a model of the SEB process, (b) validating this model with the experimental results of Guha and Jaffé (1996a,b) and Guha (1996), and (c) using the validated model to investigate the operational regime of the SEB process.

Summary of Results for Reporting Period

1. Bioavailability Analysis

The surfactant enhanced bioavailability of phenanthrene was analyzed for systems with soil. This analysis builds on the bioavailability analysis performed earlier, where the bioavailability equations have now been modified to account for the results of Guha and Jaffé (1996a,b). Three cases were examined:

1. The total phenanthrene in the system is below the aqueous solubility limit (0.73 mg/L of phenanthrene in a soil-slurry reactor with 5% w/w soil which has a 2.6% organic carbon content - these are the experimental conditions of Guha (1996)).

2. The total phenanthrene in the system is above the aqueous solubility limit, but the aqueous phenanthrene concentration is below the solubility limit due to phenanthrene sorption to the soil. (14 mg/L of phenanthrene in the soil-slurry reactor)

3. The total phenanthrene in the system is sufficient to maintain the aqueous phenanthrene concentration at the solubility limit (25 mg/L of phenanthrene in the soil-slurry reactor).

The following conclusions can be made from the analysis presented in Figure 2:

1. There is an optimal surfactant range for enhanced bioavailability. The location of this range depends on the CMC (shifts due to surfactant sorption to the soil), and the width of the range depends on the shape of the micellar-phase bioavailability factor (Figure 1b).

2. Surfactant-enhanced bioavailability (which is defined as a bioavailability greater than the aqueous contaminant concentration when there is no surfactant present) occurs under all three cases of Figure 2. While there is enhanced bioavailability through the addition of surfactants to a soil-slurry system under all cases, it is most pronounced when the total phenanthrene concentration in the system is greater than the solubility limit. However, if there is a minimum substrate concentration required for bacteria to degrade a contaminant, surfactant-enhanced bioavailability may provide a means to biodegrade to a level lower than that possible without surfactants.

3. While the surfactant concentration range for enhanced bioavailability is a function of the total phenanthrene concentration, the surfactant concentration giving the maximum phenanthrene bioavailability is independent of the phenanthrene concentration. For the conditions in Figure 2, the optimal surfactant concentration is approximately 800 mg/L.

2. Biodegradation Enhancement Analysis

While above results show that there is a surfactant concentration region which provides an enhanced bioavailability, it remains to be seen if the bacteria are capable of utilizing the increase in bioavailable phenanthrene. To address this issue, we start with the Monod equation:

$$\mu = \mu_{max} \frac{C_{bio}}{K_s + C_{bio}} \tag{1}$$

Here, μ is the biomass growth rate, μ_{max} is the maximum biomass growth rate, C_{bio} is the bioavailable HOC concentration, and K_s is the Monod half saturation coefficient. It can be seen from Eqn. 1 that if C_{bio} is

much greater than K_s, then the bacteria are growing at their maximum rate. Thus, any further improvement in the bioavailable concentration will have negligible effect on the overall biodegradation rate. In order to assess the effect of surfactant addition on the growth rate (i.e., HOC degradation rate), we can define the percent improvement in biodegradation rate as

$$I = \left\{ \frac{\left(\dfrac{C_{bio}}{K_s + C_{bio}} \right)}{\left(\dfrac{C_{aqueous}}{K_s + C_{aqueous}} \right)} - 1 \right\} \cdot 100\% \qquad (2)$$

where $C_{aqueous}$ is the aqueous phenanthrene concentration without any surfactant present, and I is the percent improvement in biodegradation rate through the addition of surfactant. Eqn. 2 gives us a method to judge the relative improvement in biodegradation rate through the addition of surfactant. For example, the percent improvement in biodegradation rate for the conditions of Figure 2(b) shown in Figure 3 suggests that the largest improvements in biodegradation rate will be realized with bacteria that have a high K_s coefficient.

Figure 3 also suggests that for lower K_s values, there is no significant advantage in increasing the bioavailable concentration beyond a certain value. If we look at a $K_s = 0.6$ mg/L in Figure 3, we see that there is no significant advantage in improving the bioavailable concentration above ~2 mg/L. Figure 4 shows the results of a model run for this case. It is seen in Figure 4 that the optimal surfactant regime which results in improved biodegradation appears to be somewhat flatter than that suggested by the bioavailable concentration shown in Figure 3(b). This is due to the effects of K_s and C_{bio} on I (Eqn. 2), as depicted in Figure 3. Figure 4 does show that the optimal surfactant concentration is approximately 800 mg/L, as suggested by Figure 2. The analysis outlined in Figures 3 and 4 allow the following conclusions:

- Once the bioavailable factor equation has been determined (f_g in Figure 1b), the optimal surfactant concentration for enhanced biodegradation of a soil-slurry system can be chosen from data obtained from simple sorption and solubility experiments. Thus, the results of Figure 2 can be used to choose the optimal surfactant concentration, rather than performing numerous biodegradation experiments to provide the data similar to Figure 4.

- The actual choice of surfactant concentration will depend on the relationship between K_s and C_{bio}, as described by Eqn. 2 and Figure 3. Enhancement beyond any effective increase in the biodegradation rate will only serve to increase surfactant costs without any improvement in degradation.

- The time required to degrade the HOC must still be assessed through a complete simulation with knowledge of all the relevant parameters.

3. Presentation to the Fourth International In Situ and On-Site Bioremediation Symposium

A poster of the work performed under this contract was presented at the Fourth International In Situ and On-Site Bioremediation Symposium, New Orleans, April 28 - May 1 1997. The poster and extended abstract (which was published in the symposium proceedings) are attached as Appendices A and B, respectively.

Planned Effort

A no-cost extension has been requested to address transport issues in the presence of surfactants, non-aqueous phase liquids, and trace metals. This knowledge is required for the design of surfactant-enhanced site remediations containing complex wastes.

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Aronstein, B. N., Y. M. Calvillo, and M. Alexander. 1991. "Effect of Surfactants at Low Concentrations on the Desorption and Biodegradation of Sorbed Aromatic Compounds in Soil". *Environ. Sci. Technol.* 25:1728-1731.

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Ellis, W. D., J. R. Payne, and G. D. McNabb. 1985. "Treatment of contaminated soils with aqueous surfactants". EPA-600/2-85/129, U.S. EPA, Cincinati, OH.

Guha, S., 1996. Ph.D. Dissertation, "Surfactant enhanced bioremediation: Bioavailability of hydrophobic organic compounds partitioned into the micellar phase of nonionic surfactants." Princeton University
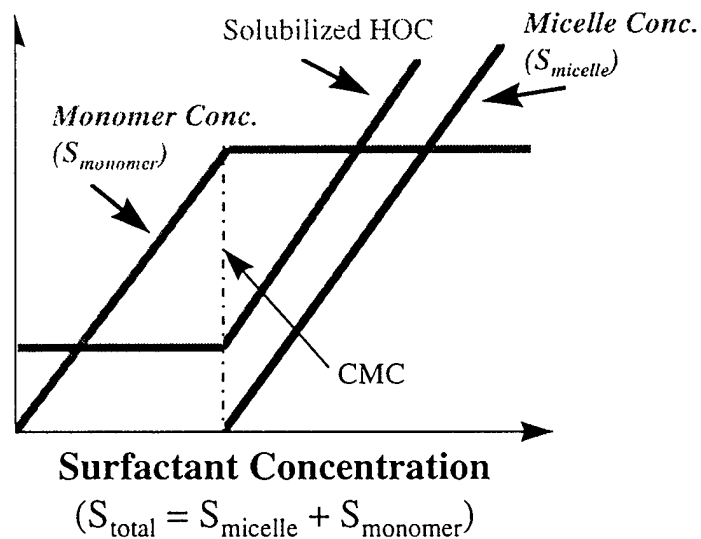
Guha, S. and P.R. Jaffé. 1996a. "Biodegradation kinetics of phenanthrene partitioned into the micellar phase of nonionic surfactants." Env. Sci. and Tech., 30(2):605-611.

Guha, S. and P.R. Jaffé. 1996b. "Bioavailability of hydrophobic compounds partitioned into the micellar phase of nonionic surfactants." Env. Sci. and Tech., 30(4):1382-1391.
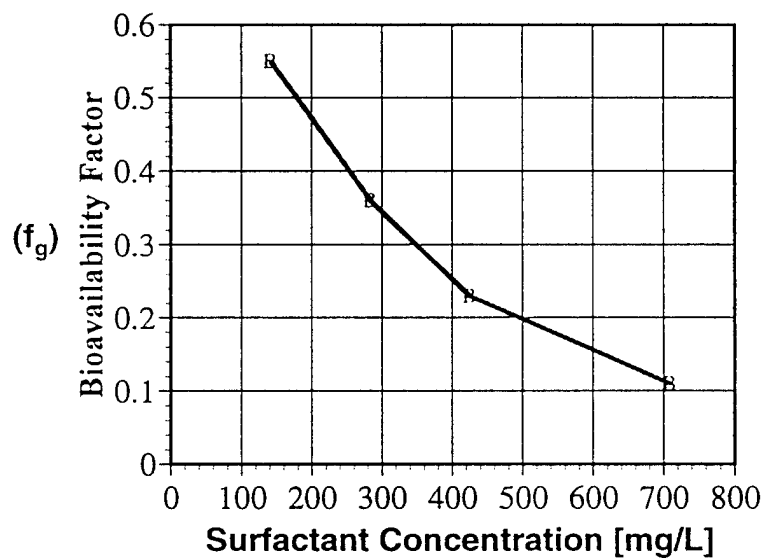
Laha, S., and R. G. Luthy. 1991. "Inhibition of Phenanthrene Mineralization by Nonionic Surfactants in Soil-Water Systems". *Environ. Sci. Technol.* 25:1920-1930.

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Solubilized HOC

Micelle Conc.
$(S_{micelle})$

Monomer Conc.
$(S_{monomer})$

CMC

Surfactant Concentration

$(S_{total} = S_{micelle} + S_{monomer})$

(a)

(b)

FIGURE 1. (a) The addition of surfactant to an aqueous system results in the formation of micelles when the aqueous surfactant concentration is above the Critical Micelle Concentration (CMC). A micelle consists of surfactant molecules arranged such that the hydrophobic portion of the surfactant molecules is in the inside of the micelle. This hydrophobic core of the micelle gives a hydrophobic organic compound (HOC) an additional "site" to partition into, increasing the effective HOC solubility. (b) Guha and Jaffé (1996a,b) and Guha (1996) showed that a fraction of the micellar-phase HOC is bioavailable, and that the micellar-phase bioavailability decreases with increasing surfactant concentration. Here, f_g is the fraction of micellar-phase phenanthrene that is bioavailable with Triton N-101 as the non-ionic surfactant.
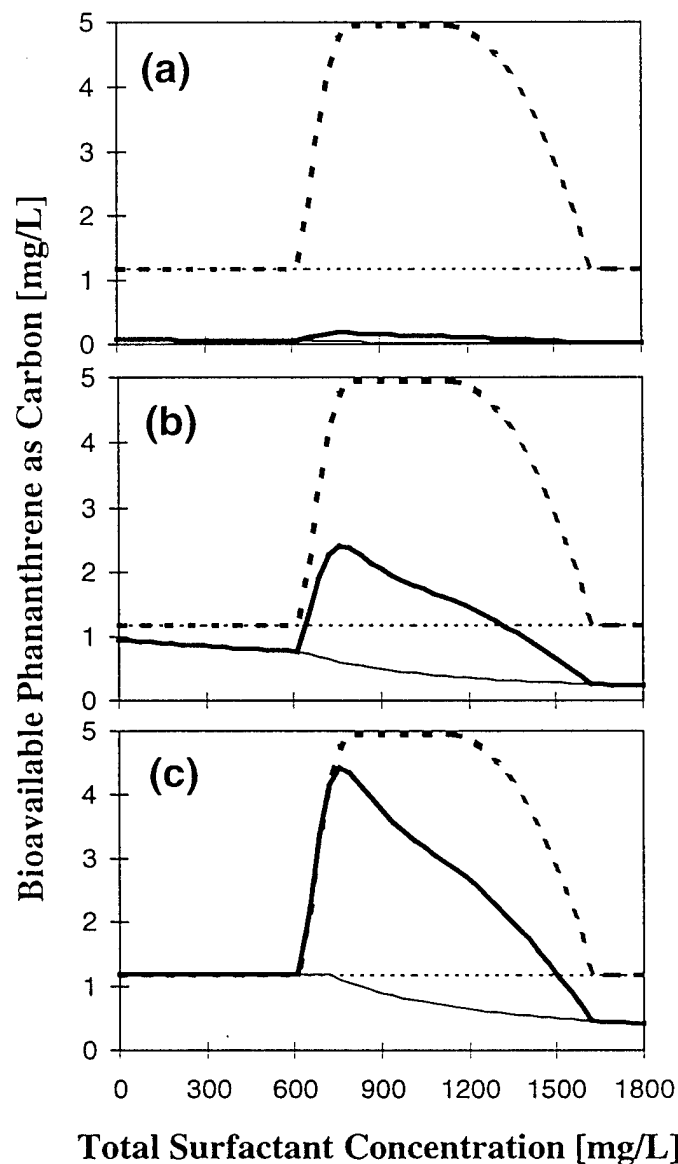
FIGURE 2. Bioavailable phenanthrene concentration as a function of surfactant concentration resulting from the interaction between bioavailability and solubility (see Figure 1). The bold dashed line in all the figures is the maximum bioavailability curve (MBC), which occurs if there is an "infinite" source of phenanthrene available. The lighter dashed line is the aqueous phenanthrene concentration for the MBC (for the MBC, it remains at the phenanthrene solubility limit). The bold solid lines are the bioavailable concentrations at specified phenanthrene concentrations, and the light solid lines are the aqueous phenanthrene concentrations. The curves have total phenanthrene concentrations as carbon of (a) 0.73 mg/L, which is the experimental condition used in Guha (1996), (b) 14 mg/L, and (c) 25 mg/L. Surfactant is Triton N-101, soil (5% $^w/_w$) with an organic fraction of 2.6%. For discussion, see text.
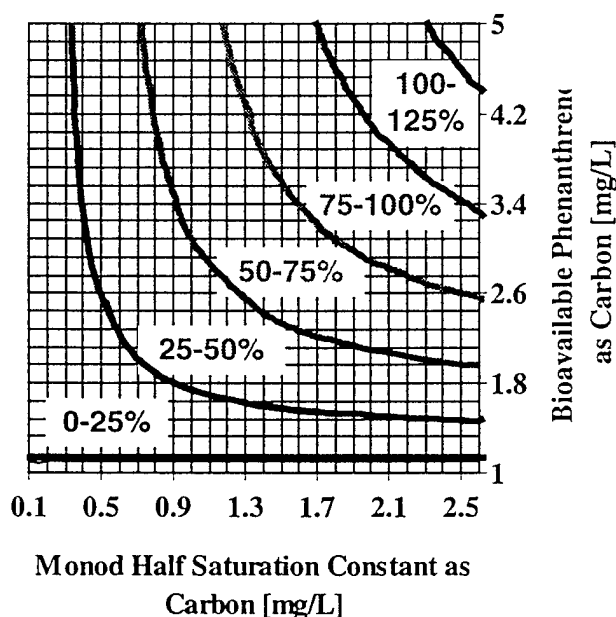
FIGURE 3. Percent improvement in biodegradation rate as compared to the aqueous phenanthrene concentration prior to addition of surfactant, as obtained from Eqn. 2. Results are for the case of Figure 2(b), where the aqueous phenanthrene concentration is approximately 1 mg/L as carbon.
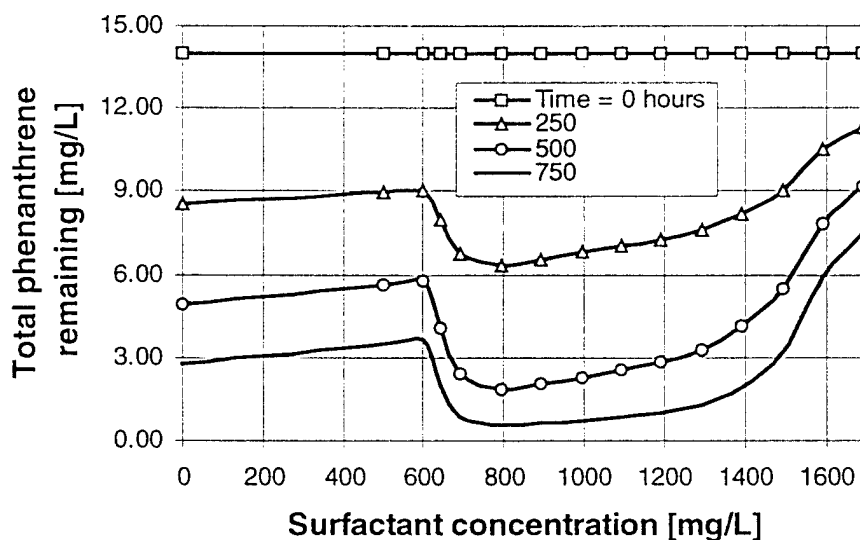

FIGURE 4. Model results for surfactant-enhanced biodegradation of phenanthrene show that there is an optimal surfactant range for enhanced biodegradation. The conditions are for those presented in Figure 2(b), with K_s = 0.6 mg/L as carbon. All remaining parameters are identical to those determined experimentally by Guha (1996), with the exception that the endogenous respiration coefficient is 0.0005 hr^{-1}. For further discussion, see text.

Appendix A

Poster Paper Presented at the
Fourth International In Situ and On-Site Bioremediation Symposium,
New Orleans, April 28 - May 1 1997.

Modeling Biodegradation of Phenanthrene in the Presence of Non-Ionic Surfactant

Derick G. Brown, S. Guha, and P. R. Jaffé

Princeton University, Princeton, NJ

Outline of Poster Presentation

- Introduction (2-4)

- Goals and Approach (5-6)

- Model Description (7-9)

- Model Validation (10-13)

- Analyses and Results (14-20)

- Conclusions (21)

References:

Edwards, D. A., Z. Adeel, and R. G. Luthy. 1994. "Distribution of Nonionic Surfactant and Phenanthrene in a Sediment/Aqueous System". *Environ. Sci. Technol..* **28**:1550-1560.

Guha, S., 1996. Ph.D. Dissertation, "Surfactant enhanced bioremediation: Bioavailability of hydrophobic organic compounds partitioned into the micellar phase of nonionic surfactants." Princeton University.

Guha, S. and P.R. Jaffé. 1996a. "Determination of monod kinetic coefficients for volatile hydrophobic compounds." *Biotech. Bioeng.* 50(7):693-699.

Guha, S. and P.R. Jaffé. 1996b. "Biodegradation kinetics of phenanthrene partitioned into the micellar phase of nonionic surfactants." *Environ. Sci. Technol.,* 30(2):605-611.

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Guha, S., D.G. Brown, and P.R. Jaffé. 1997. "Bioremediation of a PAH in soil slurry rectors using surfactants." *J. Env. Eng.,* Submitted for publication.
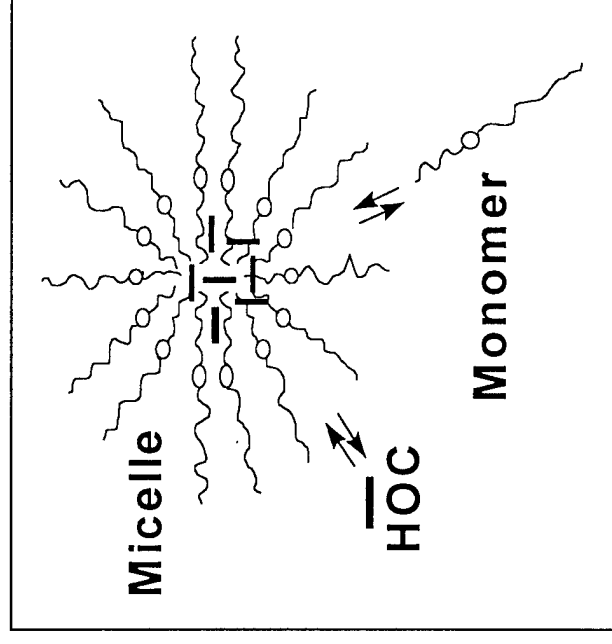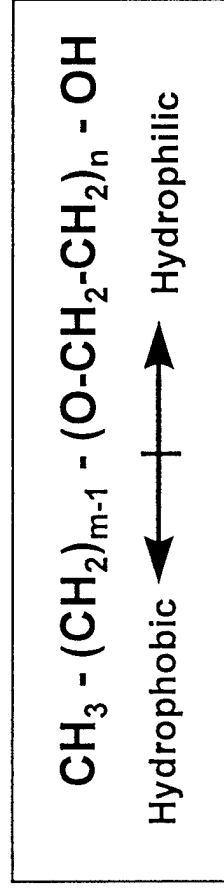
Derick G. Brown   PrincetonUniversity

Amphiphilic structure of surfactants results in the formation of micelles

$$CH_3 - (CH_2)_{m-1} - (O-CH_2-CH_2)_n - OH$$

Hydrophobic ◀━━━━▶ Hydrophilic

Micelle

Monomer

HOC

- Surfactants will form micelles at concentrations above the critical micelle concentration.

- Micelles have a hydrophobic core into which hydrophobic organic compounds (HOC's) can "partition."
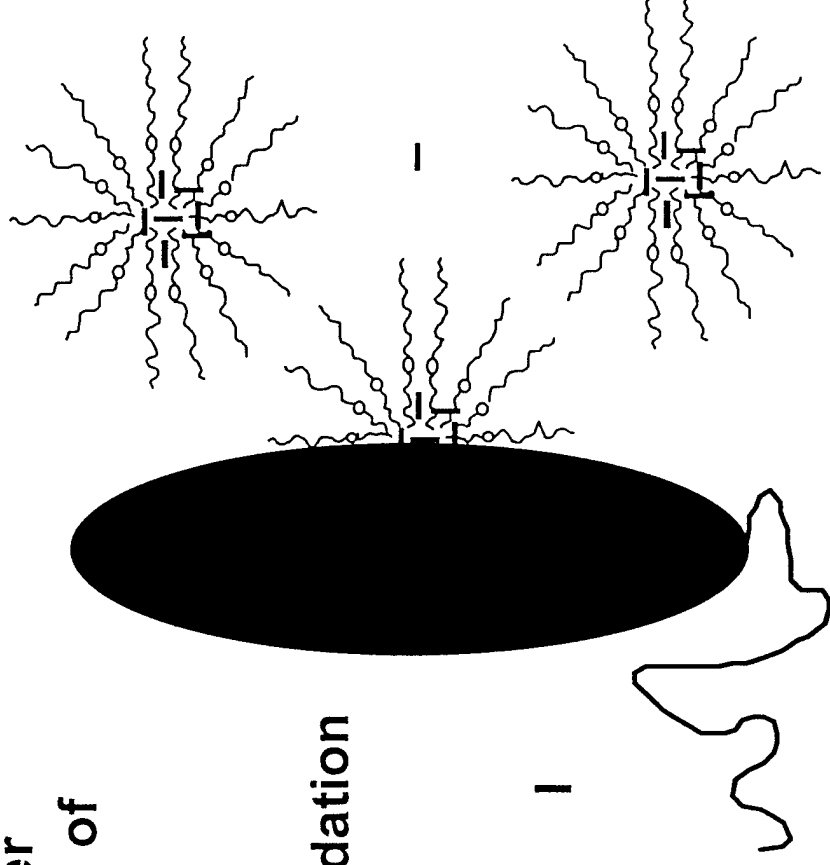
Surfactant micelles have the potential to enhance biodegradation of HOC's

Low water solubility of HOC's prevents effective biodegradation

Addition of surfactant:

- Significantly increases effective aqueous solubility of HOC's

- Shows promise in enhancing HOC biodegradation

Derick G. Brown

PrincetonUniversity

A fraction of the micellar phase HOC is biodegradable

Triton N-101

Bioavailability Factor (f_g)

Surfactant Concentration [mg/L]

- Guha and Jaffe (1996b,c) showed that a fraction (f_g) of the micellar phase HOC (C_{mic}) is bioavailable.

- The bioavailable HOC (C_{bio}) is therefore a function of the aqueous HOC concentration (C_{aq}) and the surfactant concentration (S).
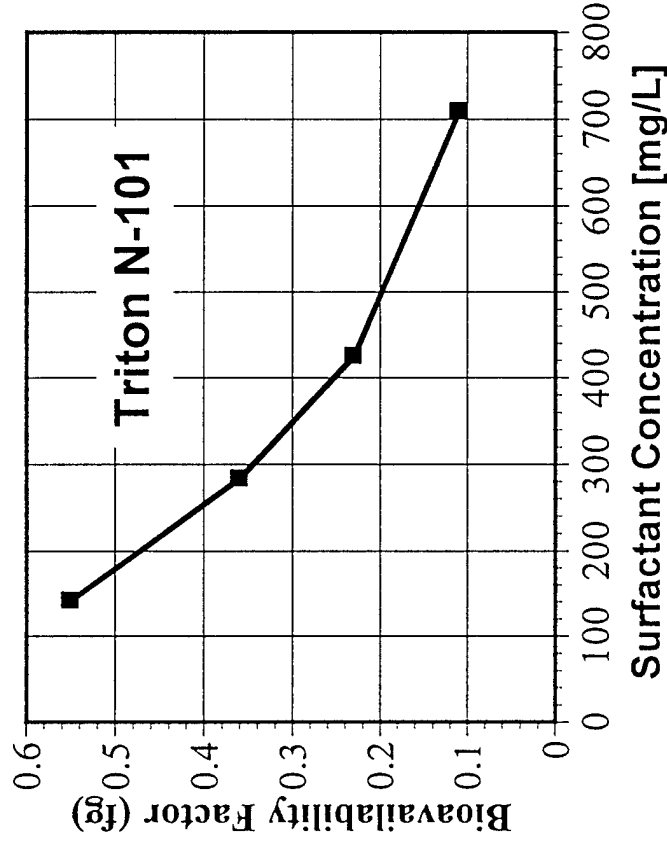
$$C_{bio} = C_{aq} + f_g(S) \cdot C_{mic}(S)$$

# There are a number of research questions which need to be addressed

- Is there an optimal surfactant concentration or concentration range for enhanced bioavailability?

- How does the total amount of HOC in the system affect bioavailability?

- Under what conditions is surfactant enhanced biodegradation feasible?

Purpose is to improve our understanding of the surfactant enhanced bioremediation (SEB) process
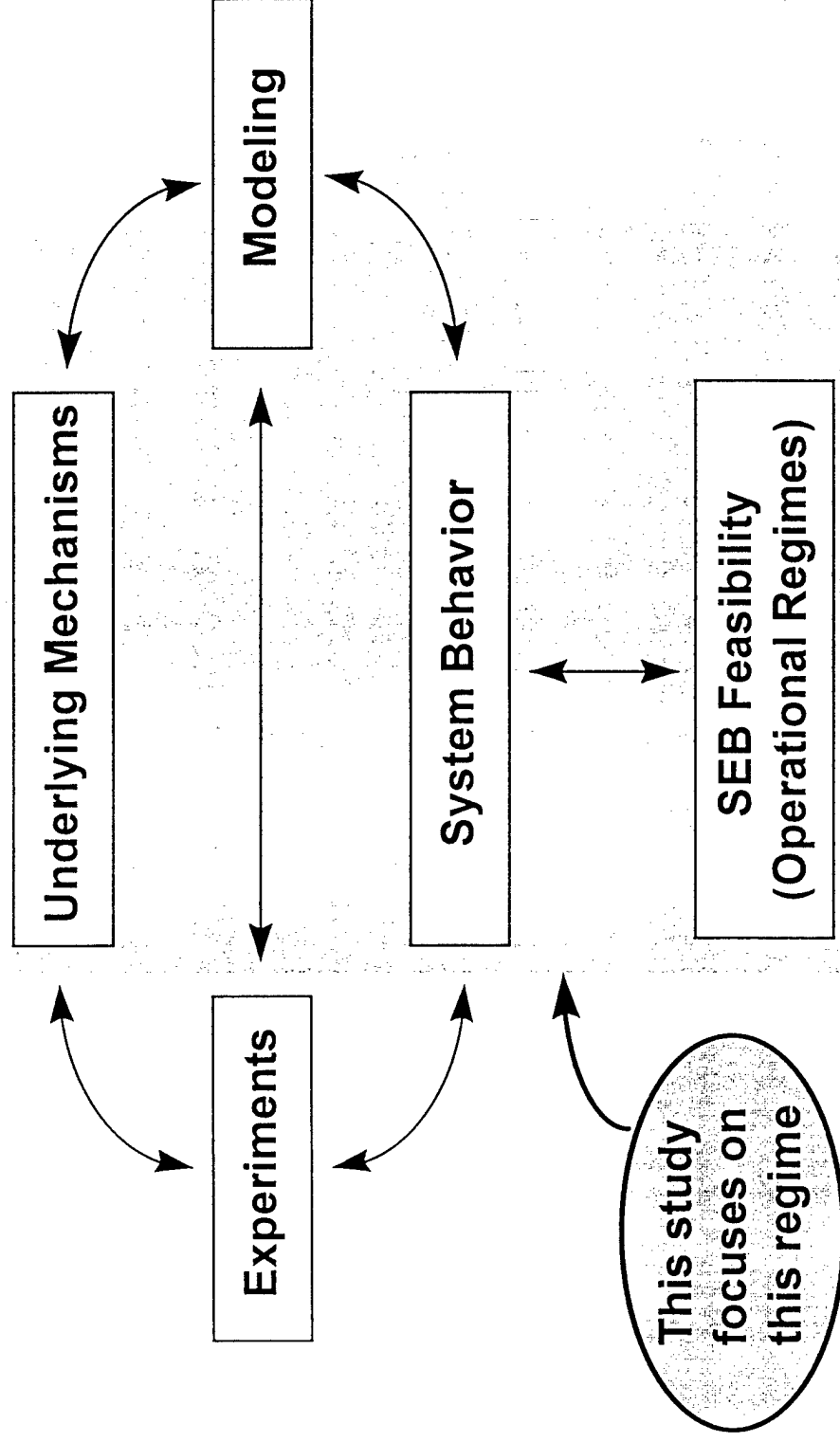
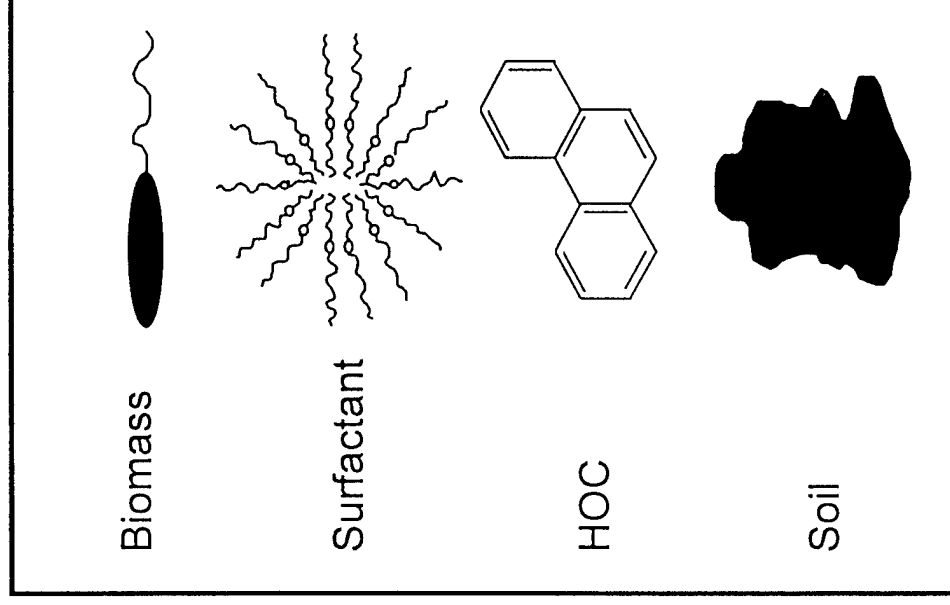# Model accounts for interactions between four main components

Assumptions

- Batch Reactor.

- System is assumed to be completely mixed, so that transport is not rate limiting.

- Surfactant does not affect kinetics of HOC biodegradation.

- Surfactant does not affect the mass transfer coefficient of the sorbed HOC.

- Only aqueous and micellar phase HOC are biodegraded.

Biomass

Surfactant

HOC

Soil

A Number of HOC-surfactant-soil Interactions are Accounted for in the Model

Micelle

k_{mic}

Monomer

k_{surf}

Soil Particle

k'_p, k_d, F

Hydrophobic Organic Compound

Two site sorption model

Modified equilibrium partition coeff [Edwards et al., 1994].

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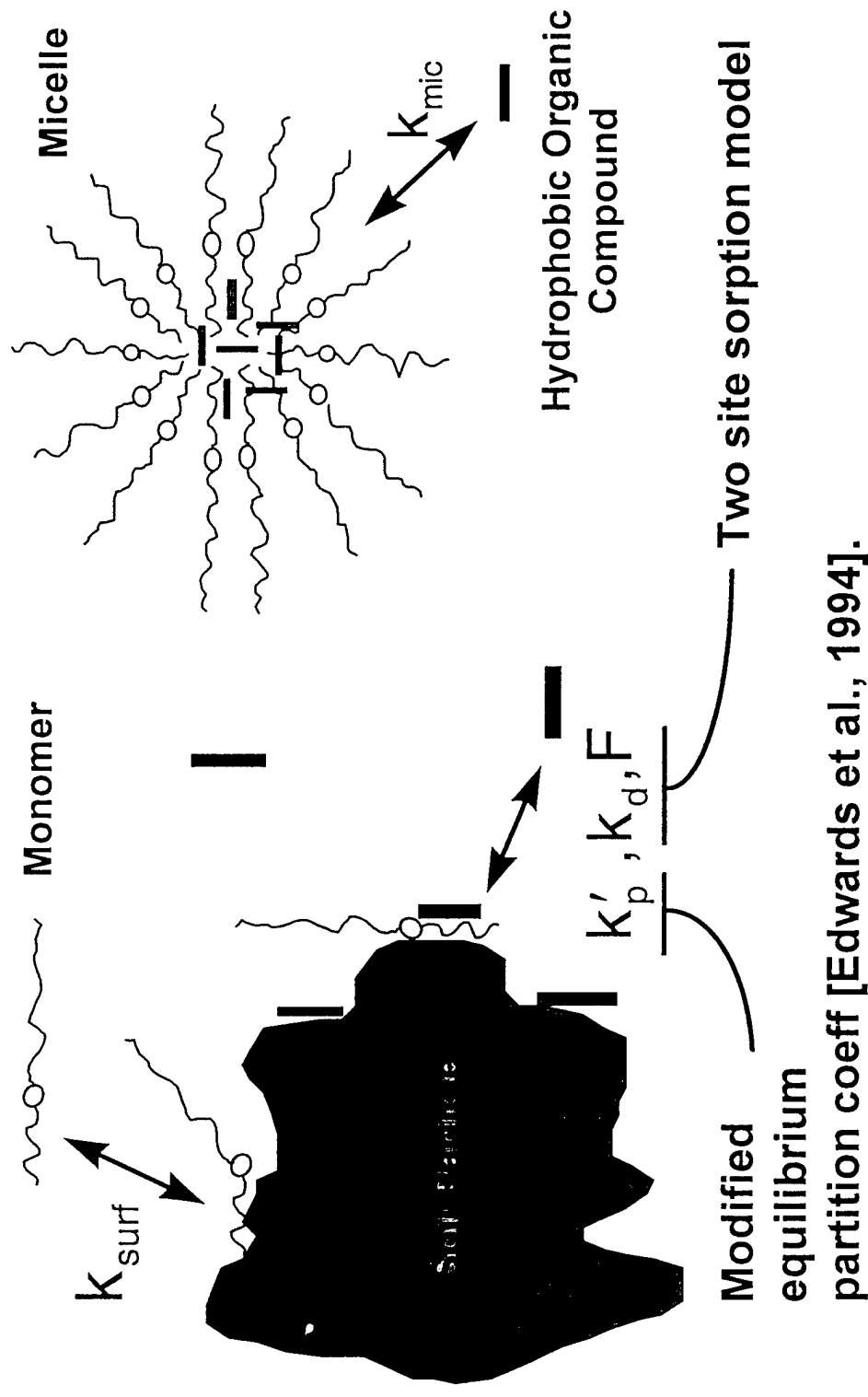
The Model Contains Three Major Terms for the HOC Mass Balance

Sorption (Two-Site)

$$S_2 \xleftrightarrow{k_d} C \xleftrightarrow{F,k'_p} S_1$$
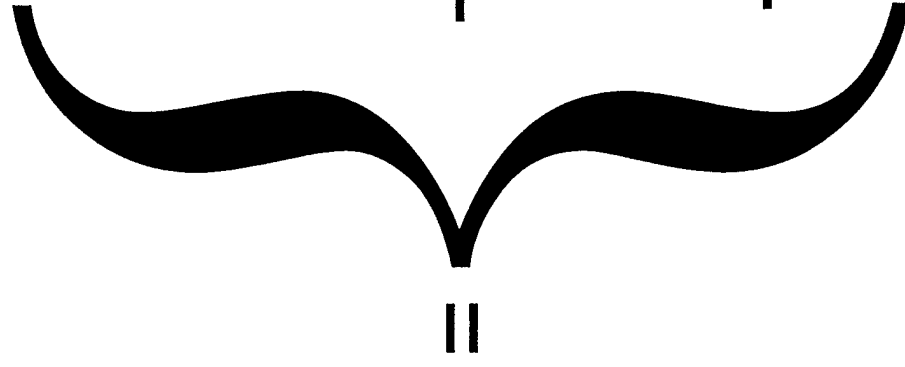
Biodegradation (Monod)

$$\mu = \mu_{max} \frac{C_{bio}}{K_s + C_{bio}}$$

Volatilization (Henry's Law)

$$K_{wg}, K_H$$

Accumulation

$$R\frac{dC}{dt}$$

$$R\frac{dC}{dt} = \{ \text{Sorption} \} - \{ \text{Biodegradation} \} - \{ \text{Volatilization} \}$$

Model verified against experimental data

- Model parameters were determined from independent experiments.

- Model verified with experimental results

  - Desorption experiments

  - Biodegradation experiments without soil

  - Biodegradation experiments with soil (equilibrium HOC partitioning)

  - Biodegradation experiments with soil (rate-limited HOC desorption)

- Experimental data from Guha (1996), Guha and Jaffe (1996a,b,c), and Guha et al. (1997).

Model Parameters

Parameter Description	Value	Reference
Apparatus partition coefficient, k_{dg}	0.2384	Guha and Jaffé (1996a), Guha (1996)
Biomass partition coefficient, $k_{biomass}$	0.0137 L/mg	Guha and Jaffé (1996a), Guha (1996)
Micellar partition coefficient, k_{mic}	0.0362 L/mg	Guha and Jaffé (1996b), Guha (1996)
Critical micelle concentration, CMC	31.3 mg/L	Guha and Jaffé (1996b), Guha (1996)
Fraction of desorption sites at equilibrium, F	0.75 (no surfactant)	Guha et al. (1997), Guha (1996)
	0.70 (with surfactant)	Guha et al. (1997), Guha (1996)
Desorption rate from the non-equilibrium sites, k_d	0.005 hour^{-1}	Guha et al. (1997), Guha (1996)
Contaminant partition coefficient onto soil, k_p	0.000388 L/mg	Guha et al. (1997), Guha (1996)
Surfactant partition coefficient onto soil, k_{surf}	0.3786 L/g	Guha et al. (1997), Guha (1996)
Volatilization rate constant, K_{wg}	0.03 hour^{-1}	Guha and Jaffé (1996a), Guha (1996)
Volatilization equilibrium constant, K_H	0.48	Guha and Jaffé (1996a), Guha (1996)
Maximum specific substrate utilization rate, μ_{max}	0.001104 hour^{-1}	Guha and Jaffé (1996a), Guha (1996)
Monod half-saturation constant, K_s	0.09 mg/L	Guha and Jaffé (1996a), Guha (1996)
Yield coefficient, Y	0.39	Guha and Jaffé (1996a), Guha (1996)
Endogenous respiration coefficient, b	0.0016 hour^{-1}	Guha and Jaffé (1996a), Guha (1996)

Derick G. Brown
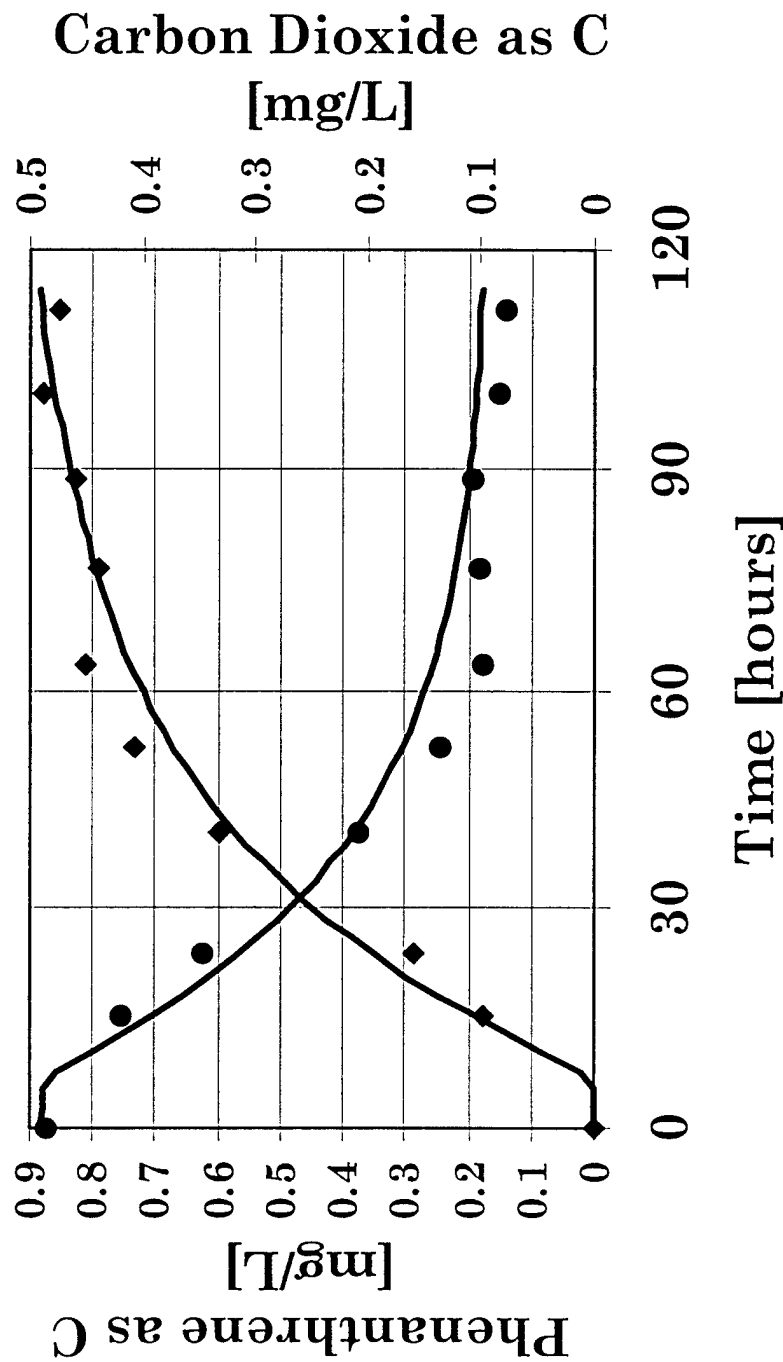
PrincetonUniversity

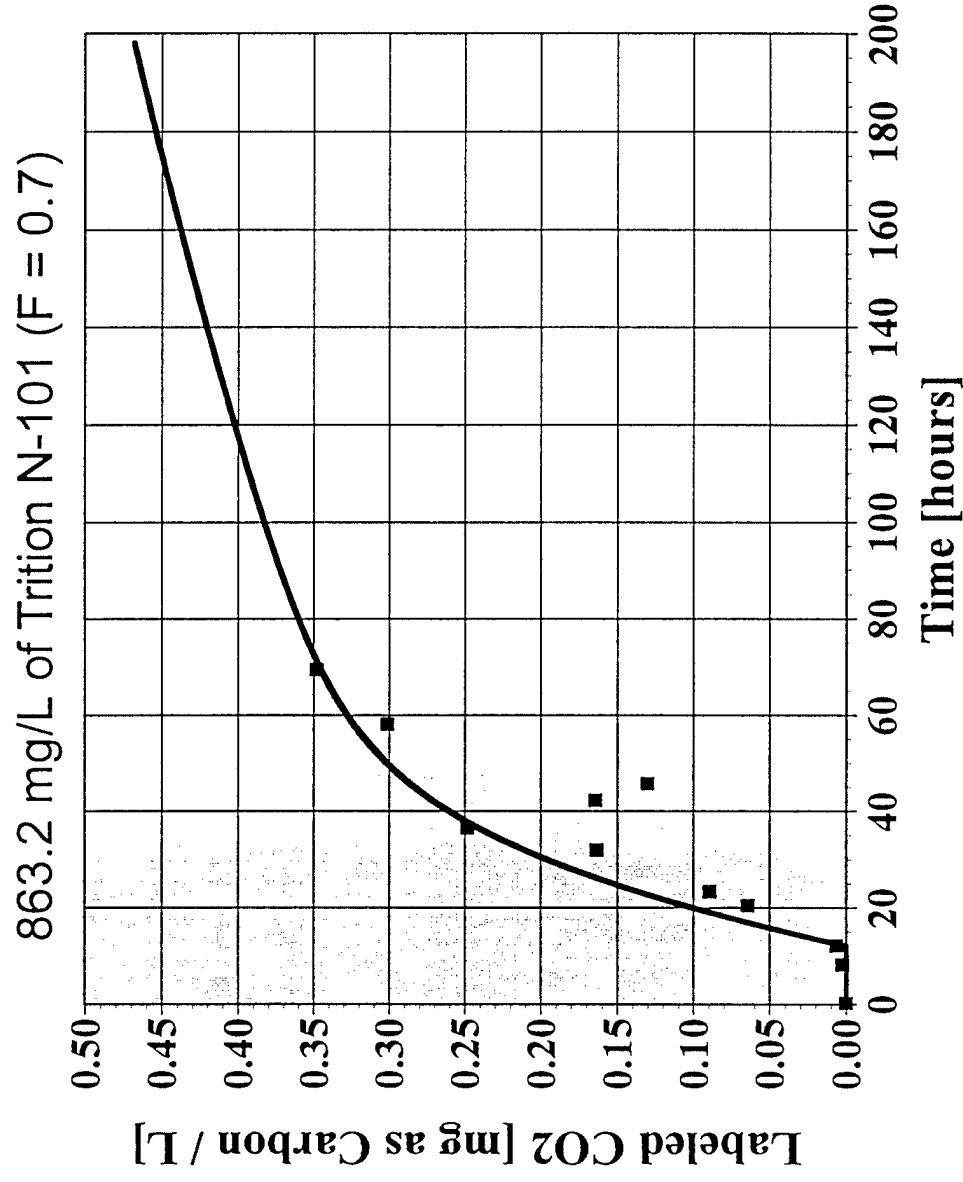# Comparision of Model Simulation to experimental results for biodegradation without soil present
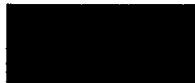
708.7 mg/L Triton N-101 (No Soil)

Comparision of Model Simulation to experimental results for biodegradation under kinetic desorption

863.2 mg/L of Trition N-101 (F = 0.7)

Labeled CO2 [mg as Carbon / L] vs Time [hours]

Derick G. Brown   PrincetonUniversity

Bioavailability of phenanthrene was examined for three cases

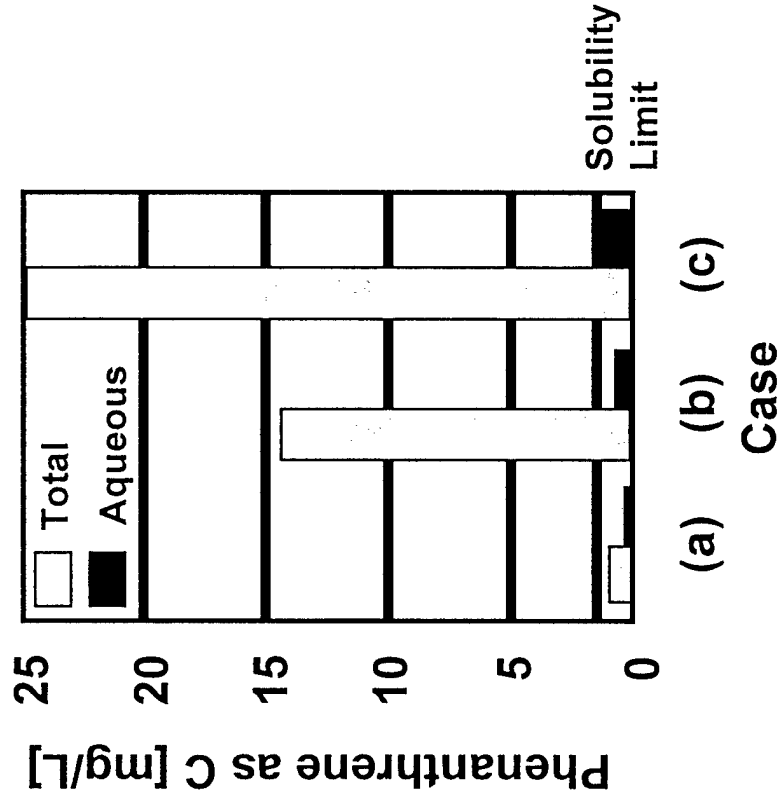**Initial Phenanthrene in System for the three test cases.**

(a) Total phenanthrene concentration always below the solubility limit (SL).

(b) Total phenanthrene above SL, but initial aqueous conc. below SL.

(c) Total phenanthrene concentration sufficient to maintain aqueous conc. at SL.

Derick G. Brown — PrincetonUniversity

Bioavailable Phenanthrene vs. Triton N-101 Concentration

Maxium bioavailability curve (MBC)

Aqueous phenanthrene conc. for MBC

Bioavailable phenanthrene for given conditions

Aqueous phenanthrene for given conditions

5% soil w/w

Total Surfactant Concentration [mg/L]

Bioavailable Phananthrene as Carbon [mg/L]

Derick G. Brown   PrincetonUniversity
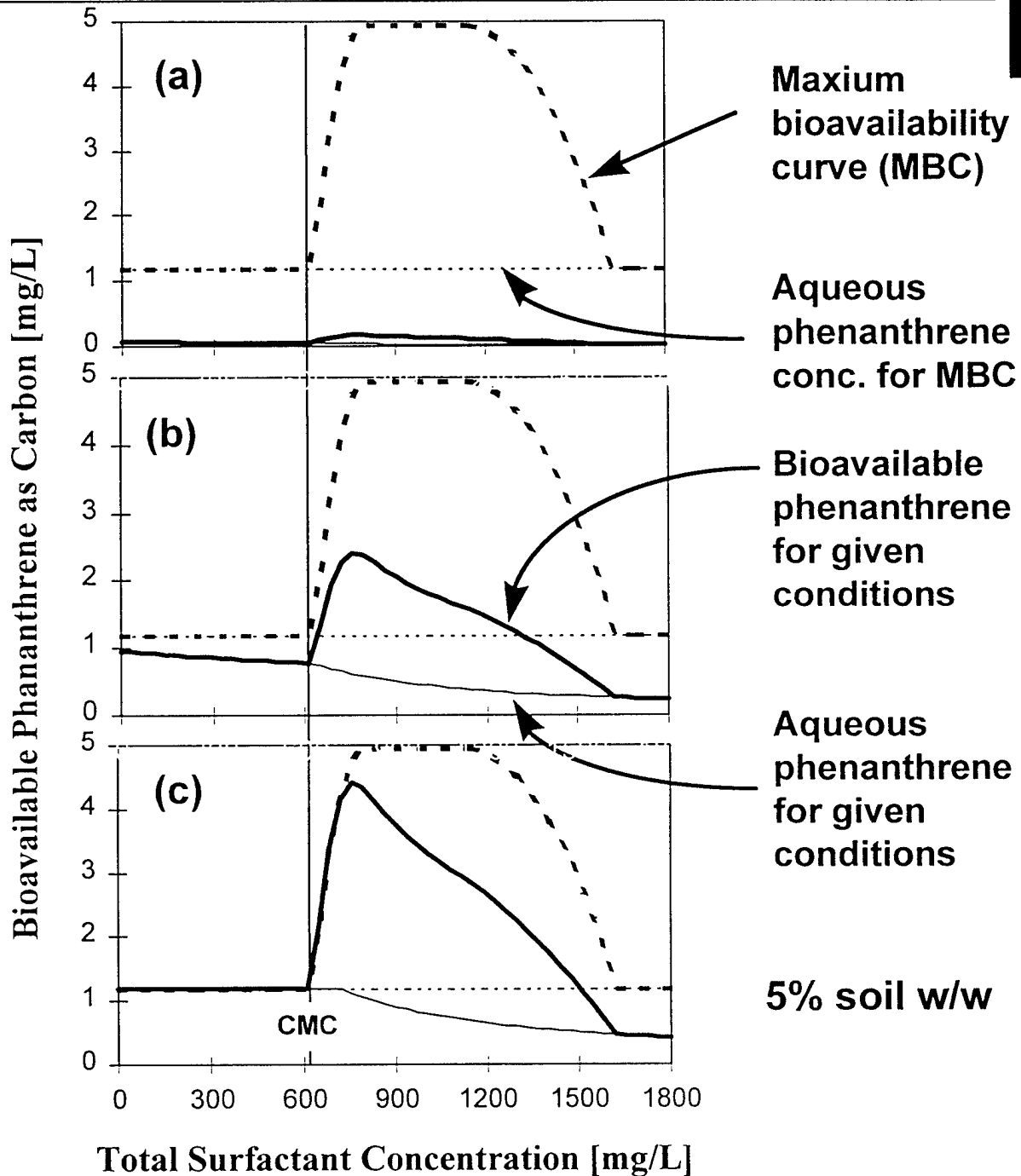
Results from bioavailability analysis

- There is an optimal surfactant range for enhanced bioavailability.

- The maximum bioavailability curve defines the maximum bioavailable concentration achievable, assuming that there is a sufficient source of HOC to maintain the aqueous concentration at the solubility limit.

- Location of optimal range depends on surfactant sorption to soil (i.e., CMC will shift).

- Surfactant enhanced bioavailability occurs for all three cases.

- Enhancement is most pronounced when the total phenanthrene concentration is greater than the solubility limit.

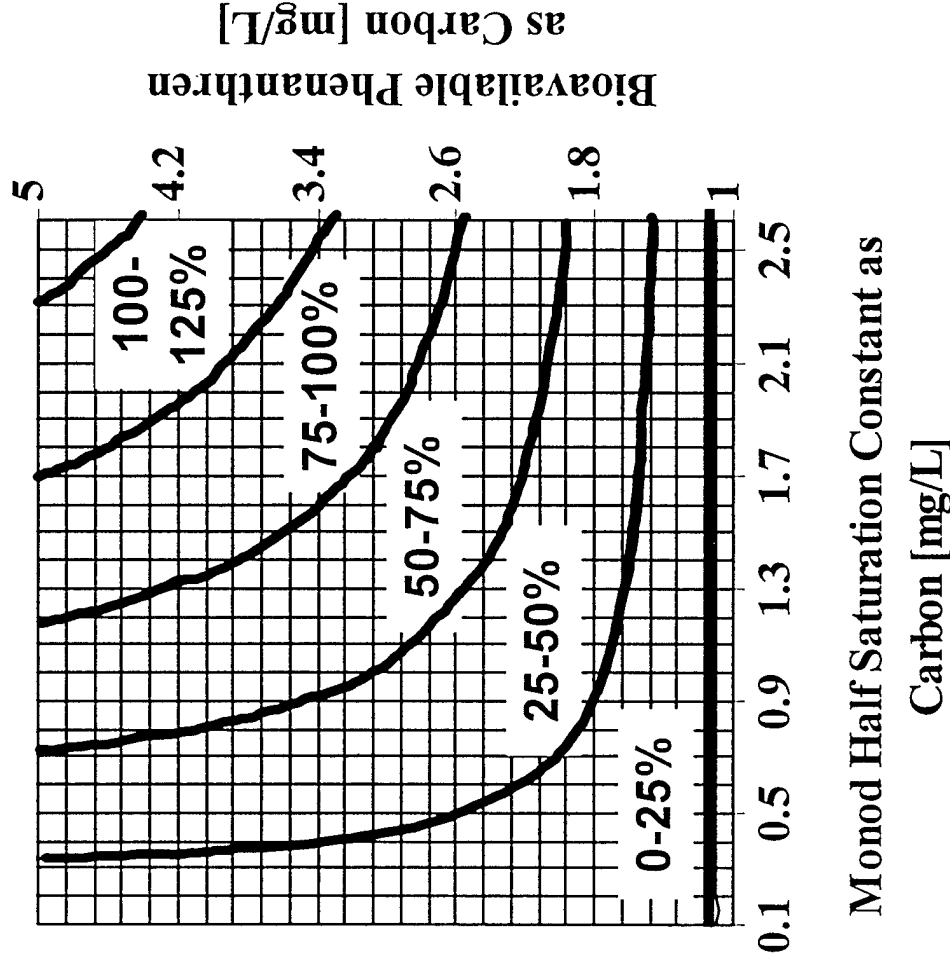- While the optimal range is a function of total phenanthrene, the optimal surfactant concentration is not.

Derick G. Brown   PrincetonUniversity

SEB is only beneficial when bacteria can utilize the increased bioavailability

Plot shows percent enhancement (I) in bacterial growth rate through addition of surfactant, where I is defined as

$$I = \frac{\left(\dfrac{C_{aq}}{K_s + C_{aq}}\right)}{\left(\dfrac{C_{bio}}{K_s + C_{bio}}\right)} - 1$$

Bioavailable Phenanthren as Carbon [mg/L]

100-125%
75-100%
50-75%
25-50%
0-25%

5 4.2 3.4 2.6 1.8 1

0.1 0.5 0.9 1.3 1.7 2.1 2.5

Monod Half Saturation Constant as Carbon [mg/L]

Results from
biodegradation ehancement analysis
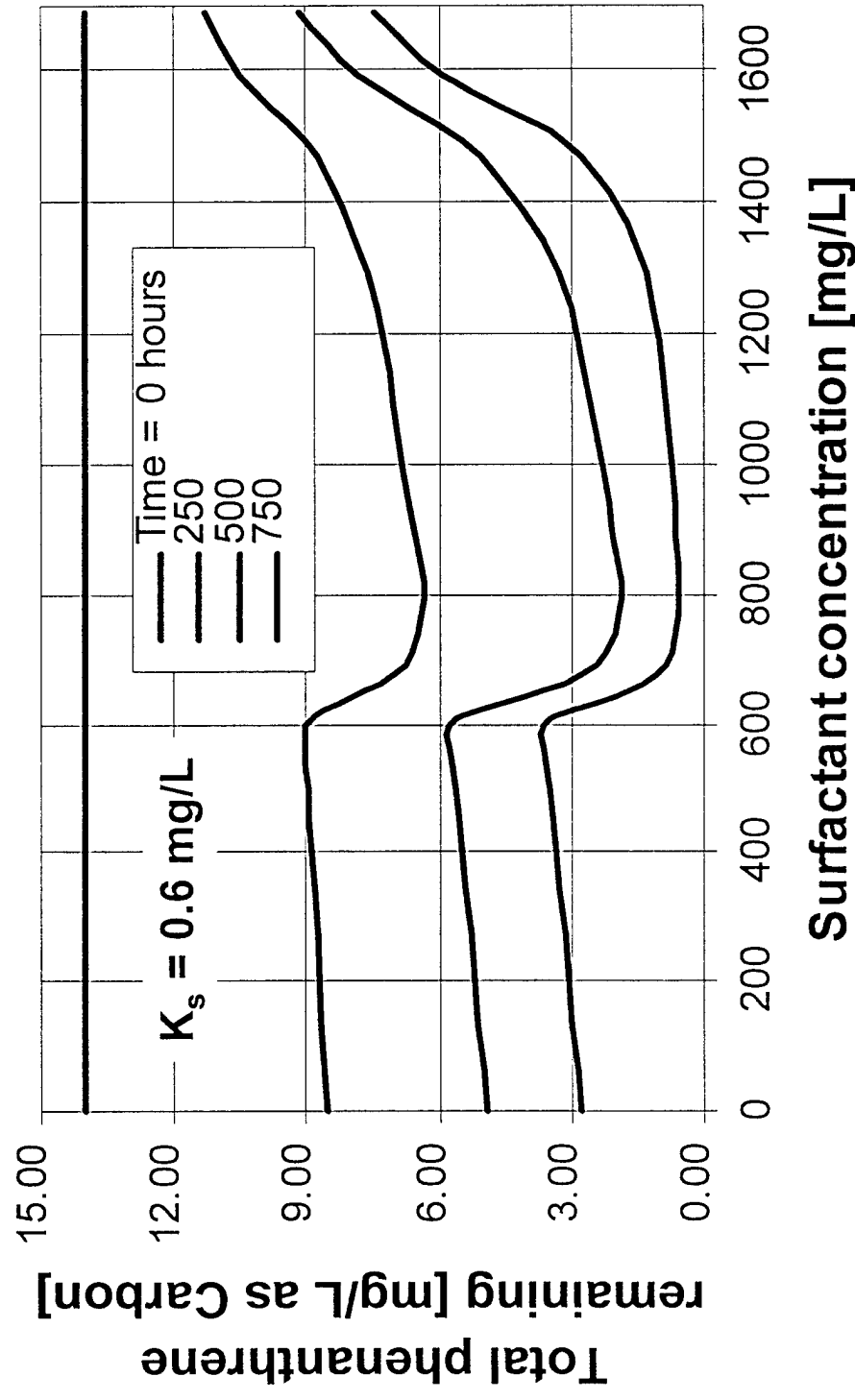
- Equation gives us a method to judge the relative improvement in biodegradation rate through the addition of surfactant.

- There is no significant advantage through addition of surfactant if bacteria have a low K_s value.

- Significant improvements in the rate of biodegradation can be achieved if the bacteria can utilize the enhanced bioavailability (i.e., the K_s value is high).

Biodegradation with rate-limited desorption for conditions of case (b)

Total phenanthrene remaining [mg/L as Carbon] vs. Surfactant concentration [mg/L]

$K_s = 0.6$ mg/L

Time = 0 hours
250
500
750

Results from biodegradation under rate-limited desorption analysis

- Figure does show that the optimal surfactant concentration is approxiately 800 mg/L, as seen in slide 15, figure (b).

- This suggests that when the bioavailability factor is known (f_g) the optimal surfactant concentration can be determined from simple sorption and solubility experiments.

- The time required to biodegrade the HOC still must be assessed through a complete simulation with knowledge of all the relevant parameters.

The results of these analyses suggest the following conclusions

- There is a surfactant range which gives enhanced bioavailability.

- Surfactant concentration giving the maximum bioavailability is independent of the HOC concentration (when there is soil in the system).

- When the bioavailability factor is known (f_g), the optimal surfactant concentration for enhanced biodegradation can be obtained from simple sorption and solubility equilibrium experiments.

- The benefit of surfactant enhanced biodegradation may be limited by the value of the Monod half-saturation constant.

Appendix B

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MODELING BIODEGRADATION OF
PHENANTHRENE IN THE PRESENCE OF NON-IONIC SURFACTANT

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ABSTRACT: A mathematical model of a soil-slurry reactor with surfactant was developed to determine the feasibility of surfactant-enhanced biodegradation of hydrophobic organic compounds (HOC). The model accounted for the biodegradation of the micellar-phase contaminant, sorption of surfactant onto soil, and rate-limited desorption of contaminant. The model results were validated against experimental results from soil-slurry reactors using phenanthrene as the model HOC with a non-ionic surfactant (Triton N-101). Utilization of this model with parameters for phenanthrene and the non-ionic surfactant Triton N-101 has shown that there is an optimal range of surfactant concentration to enhance the bioavailability of phenanthrene, and this range is a function of the phenanthrene concentration. Further, the model indicates that a significant enhancement of the biodegradation rate in a soil slurry reactor can be realized when there is non-aqueous phase HOC present in the soil matrix.

INTRODUCTION

Overview: Removal of hydrophobic organic compounds (HOC) from contaminated soils is severely affected by the low HOC water solubility and high partitioning onto the soil matrix. These same traits result in HOC having low biodegradation rates. Over the last few years attention has been focused on increasing the solubility and bioavailability of HOC with the addition of surfactants [e.g., Aronstein et al. (1991); Edwards et al. (1994); Guha and Jaffé (1996a,b); Guha (1996)]. While research has indicated that surfactants can enhance the solubility and bioavailability of hydrophobic compounds (see Figure 1), the question remains as to whether surfactant-enhanced bioremediation is a feasible process for remediation of contaminated soils.

Objective: The combination of surfactant-enhanced HOC solubilization and bioavailability shown in Figure 1 has the potential of enhancing the biodegradation of HOC; however, the interactions between the HOC solubilization and bioavailability, and effects of HOC sorption/dissolution, need to be examined in order to determine the feasibility of the surfactant-enhanced bioremediation (SEB) process. The objective of the current research is to increase our understanding of the SEB process and to identify operational regimes where the SEB process is applicable.

NUMERICAL MODEL

Mass Balances: The numerical model developed for this investigation consists of seven mass balances: aqueous HOC, sorbed HOC, volatilized HOC, extra-phase

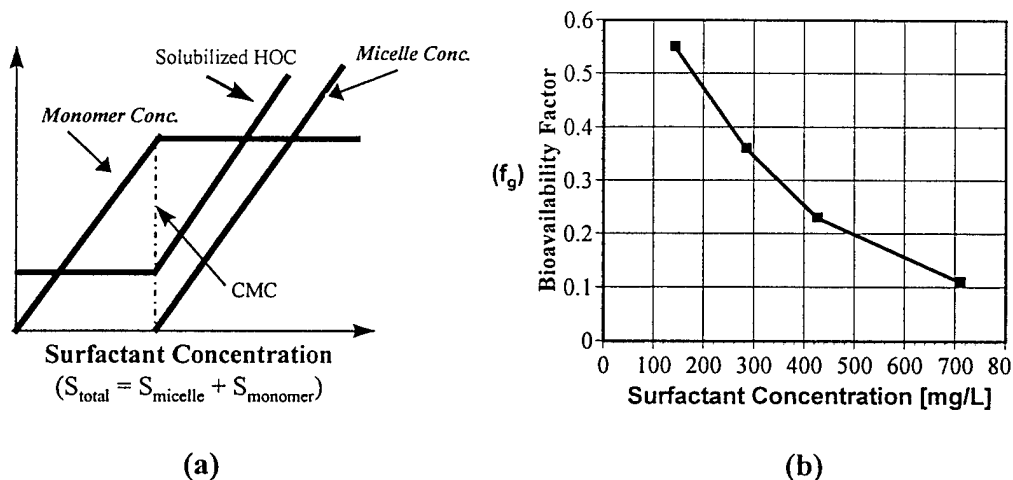(a)   (b)

FIGURE 1. (a) The addition of surfactant to an aqueous system results in the formation of micelles when the aqueous surfactant concentration is above the Critical Micelle Concentration (CMC). A micelle consists of surfactant molecules arranged such that the hydrophobic portion of the surfactant molecules is in the inside of the micelle. This hydrophobic core of the micelle gives a hydrophobic organic compound (HOC) an additional "site" to partition into, increasing the effective HOC solubility. (b) Guha and Jaffé (1996a,b) showed that a fraction of the micellar-phase HOC is bioavailable, and that the micellar-phase bioavailability decreases with increasing surfactant concentration. Here, f_g is the fraction of micellar-phase phenanthrene that is bioavailable with Triton N-101 as the non-ionic surfactant.

HOC, biomass, surfactant, and carbon dioxide production (used to compare to experimental results). HOC sorption is modeled using a two-site sorption model [Karickhoff (1980)], which assumes that a fraction of the sorption sites are available for equilibrium sorption, and the remaining sites are available for kinetic sorption. Biodegradation is modeled via the Monod equation, using the formulation of Guha and Jaffé (1996a,b) for the bioavailable HOC concentration in the presence of surfactants. Based on Guha and Jaffé (1996a), the bioavailable concentration is given by

$$
\begin{aligned}
C_{bio} &= C_{aq} + f_g C_{mic} \\
&= \left(1 + f_g S_{mic} k_{mic}\right) \cdot C_{aq} \\
&= f_{bio} C_{aq}
\end{aligned}
\tag{1}
$$

where C_{bio} is the bioavailable HOC concentration, C_{aq} is the aqueous HOC concentration, C_{mic} is the micellar-phase HOC concentration, f_g is the bioavailable fraction of the micellar phase, S_{mic} is the surfactant micellar concentration, k_{mic} is

the HOC partition coefficient into the micellar phase, and f_{bio} is the total bioavailable fraction.

For this soil slurry reactor model, it is assumed that the mixing is sufficiently vigorous such that the extra-phase HOC dissolution occurs at a faster rate than the HOC biodegradation; this allows the assumption that any extra-phase HOC present serves to maintain the aqueous HOC concentration at the solubility limit. The effect of the sorbed surfactant on the HOC soil partition coefficient of the two-site sorption model is modeled using the formulation of Edwards et. al. (1994), where the HOC soil partition coefficient is increased as a function of the carbon content of the sorbed surfactant molecules. It is assumed that the presence of surfactants does not directly affect the kinetic sorption coefficient; therefore the only effect of surfactants on the kinetic dissolution rate is due to the increased gradient from the surfactant-enhanced HOC solubility.

Validation: This model was verified against experimental data of Guha (1996) and Guha and Jaffé (1996a) for biodegradation under instantaneous and kinetically limited HOC desorption from soil under a variety of surfactant and soil conditions. The parameters used for the validation were determined through independent experiments and are described elsewhere [Guha (1996) and Guha and Jaffé (1996a)].

RESULTS AND DISCUSSION

Optimal Surfactant Concentration Under Equilibrium Desorption: In an aqueous system without any soil and with the total phenanthrene concentration at or below the solubility limit, addition of surfactant will only serve to reduce the bioavailable concentration. This is because addition of surfactant will transfer some of the aqueous phenanthrene, which is entirely bioavailable, to the micellar phase, which is only partially bioavailable. However, when the phenanthrene concentration is greater than the solubility limit (e.g., there is a sorbed phase and/or a separate phase present), addition of surfactant will increase the bioavailable concentration when under equilibrium conditions.

Figure 2 shows the bioavailable phenanthrene concentration as a function of surfactant (Triton N-101) and phenanthrene concentrations with no soil present. These curves result from the interaction of the micellar bioavailable fraction (Figure 1b), and the apparent solubility of phenanthrene (Figure 1a). For the case of 30x solubility limit in Figure 2, enough separate-phase phenanthrene is present to keep the aqueous concentration at the solubility limit for the range of surfactant concentrations examined. On this "maximum bioavailability curve", the maximum bioavailable concentration remains essentially constant in the range of 200 to 600 mg/L of surfactant.

With a lower total phenanthrene concentration, the curve breaks from the maximum bioavailability curve at the point where enough surfactant is present to cause the aqueous phenanthrene concentration to drop below solubility (i.e., all the extra phase phenanthrene has been solubilized). For the case of 10x solubility
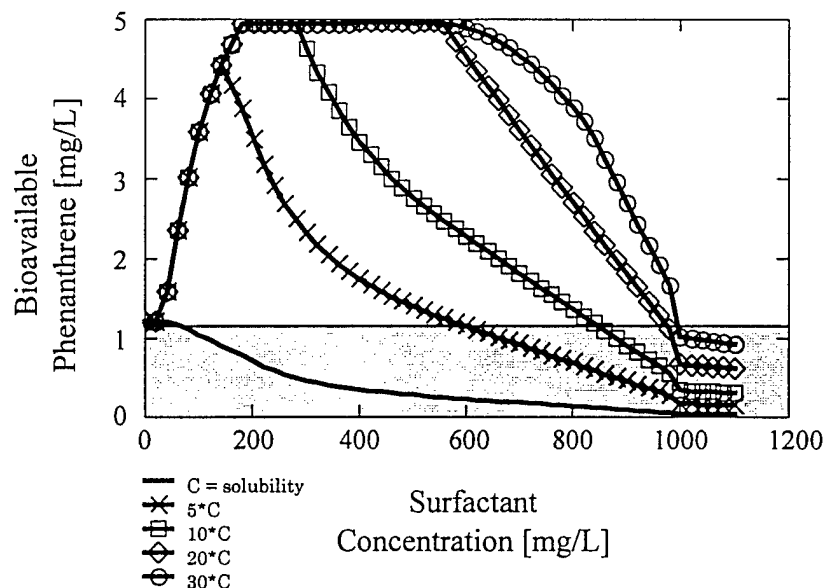
FIGURE 2. Competition between increased phenanthrene solubility and decreased micellar-phase phenanthrene bioavailability with increasing surfactant concentration (Triton N-101) results in an optimal region of enhanced bioavailability (white region, where the bioavailable concentration is greater than the aqueous solubility limit). The bioavailable concentration is given by Eqn. 1. CMC for Triton N-101 is 31.3 mg/L, and the aqueous solubility of phenanthrene is C = 1.2 mg/L as carbon [Guha and Jaffé (1996a)].

limit in Figure 2, this point occurs at a surfactant concentration of approximately 350 mg/L. For this phenanthrene concentration, the maximum bioavailable concentration is essentially constant in the range of 200 to 350 mg/L of surfactant. The implication of this shift in the optimal surfactant concentration with phenanthrene concentration is that the optimal surfactant dose will vary as the phenanthrene is degraded, ultimately requiring a zero surfactant concentration when there is no longer any separate phase phenanthrene to maintain the aqueous phenanthrene concentration at the solubility limit.

When there is soil present in the system, the whole curve in Figure 2 will shift to the right due to surfactant partitioning onto the soil. This shifting of the maximum bioavailability curve highlights the need for accurate knowledge of surfactant partitioning onto the soil. Underestimation of surfactant partitioning can result in surfactant concentrations below CMC (the curve will shift farther to the right than expected), and therefore no apparent enhancement of the bioavailable HOC. Overestimation of surfactant partitioning can result in surfactant concentrations well out of the optimum surfactant range (the curve will not shift as far to the right as expected), causing a significant reduction of the bioavailable HOC concentration and thus inhibition of the phenanthrene biodegradation.

Optimal Surfactant Concentration Under Kinetically Limited Desorption:
Figure 3 shows a model run for the biodegradation of sorbed and extra-phase
phenanthrene in the presence of Triton N-101. It can be seen in this system that
surfactants can have a significant effect on the overall biodegradation rate.
Further, Figure 3b indicates that there is an optimal surfactant concentration
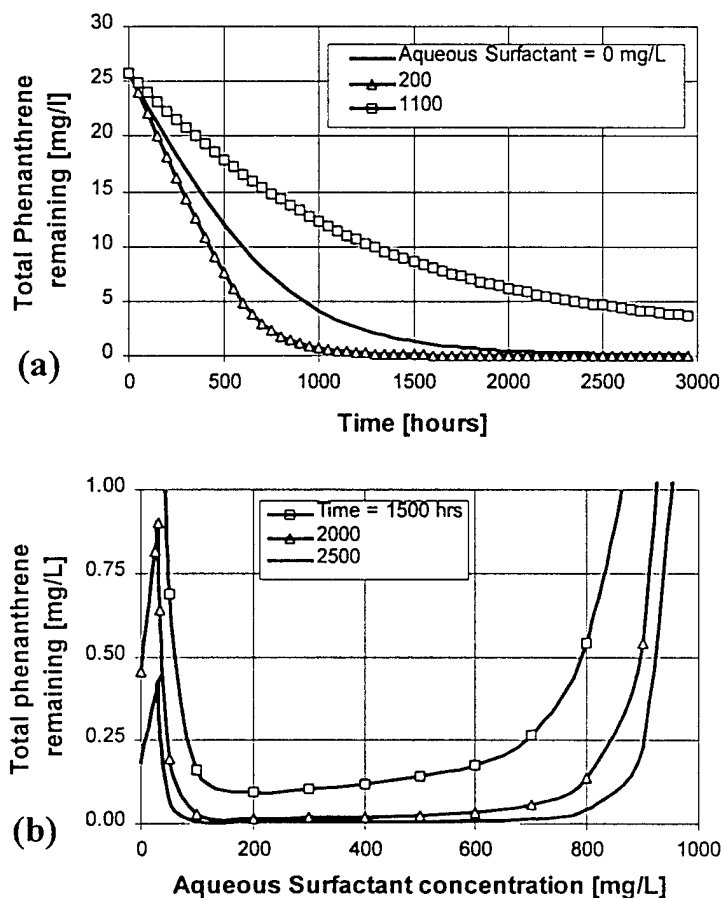within which the biodegradation rate can be maximized.

FIGURE 3. The conditions are for a soil-slurry reactor with an initial
sorbed phenanthrene concentration of 0.015 mg/g, 70% of the sites in
equilibrium sorption at a soil concentration of 50 g/L, and 0.5 mg/g of
separate phase phenanthrene present (phenanthrene concentrations
given in terms of carbon). The remaining parameters are described in
Guha (1996) and Guha and Jaffé (1996a). (a) The effects of
surfactant concentration on the bioavailability of phenanthrene
(Figure 2) are apparent in the overall biodegradation rates of
phenanthrene. (b) The model suggests that there is an optimal range
of aqueous surfactant concentration which significantly enhances the
rate of phenanthrene biodegradation.

When the conditions of Figure 3 are rerun without any extra-phase phenanthrene present, there is no significant improvement in the overall biodegradation rate (data not shown). This occurs because under the experimental conditions of Guha (1996), the biodegradation is limited by the rate of phenanthrene desorption from the soil, and thus any improvement in bioavailability via the addition of surfactant is not realized (i.e., the aqueous phenanthrene concentration falls below the solubility limit). When extra-phase phenanthrene is present, as in Figure 3, the improved bioavailability is realized, and the overall rate of biodegradation is enhanced. It should be noted that the assumption was made that surfactants do not directly affect the HOC desorption rate, and it is unclear at this time as to whether or not this is true.

In conclusion, the results of this investigation suggest that for those situations where there is extra-phase HOC present in the soil matrix, the addition of surfactants in a soil-slurry reactor has the potential to significantly increase the overall HOC biodegradation rate. When there is no extra-phase HOC present, the feasibility of surfactant-enhanced biodegradation will depend on the ratio of the biodegradation rate to the desorption rate.

ACKNOWLEDGMENTS

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